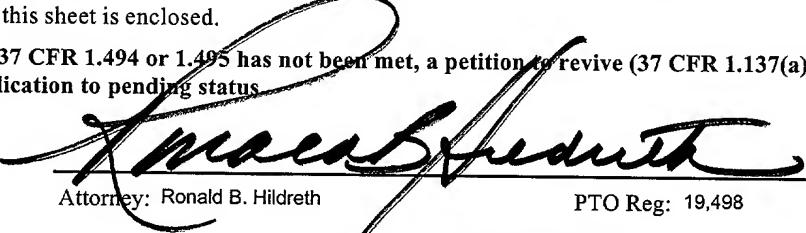


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|---|---|--|--------------------------|
| BAKER BOTTS LLP | | EXPRESS MAIL LABEL No EU206386251US | DATE 19 FEBRUARY 2002 |
| TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35.U.S.C. 371 | | ATTORNEY'S DOCKET NO. A35012 PCT USA | |
| | | U.S. APPLICATION NO. 10/049979 | |
| INTERNATIONAL APPLICATION NO. PCT/KR00/00883 | INTERNATIONAL FILING DATE 10 AUGUST 2000 | PRIORITY DATE CLAIMED 17 AUGUST 1999 | |
| TITLE OF INVENTION PHOTOSENSITIVE RESIN COMPOSITION | | | |
| APPLICANT(S) FOR DO/EO/US Yong-Sik Ahn, Kyung-Jun Kim, Yun-II Hwang | | | |
| <p>Applicant herewith submits to the United States Designated /Elected Office (DO/EO/US) the following items and other information:</p> <ol style="list-style-type: none"> <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(I). <input type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210) <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). | | | |
| <p>Items 11. to 16. below concern other document(s) or information included:</p> <ol style="list-style-type: none"> <input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409) <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. <input type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. <input type="checkbox"/> A substitute specification. <input type="checkbox"/> A change of power of attorney and/or address letter. <input checked="" type="checkbox"/> Other items or information: <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> a copy of the International Search Report (PCT/ISA/210) b. <input checked="" type="checkbox"/> a copy of the International Preliminary Examination Report (PCT/IPEA/409) | | | |
| <p>Also:</p> <p>WO 01/13175 A2 International Publication with 15 pages specification, 5 pages claims, first page with abstract PCT Demand PCT Request</p> | | | |

10/049979

JC13 Rec'd PCT/PTO 19 FEB 2002

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| INTERNATIONAL APPLICATION NO. PCT/KR00/00883 | INTERNATIONAL FILING DATE 10 AUGUST 2000 | PRIORITY DATE CLAIMED 17 AUGUST 1999 | | |
| 17. [] The following fees are submitted: | | <u>CALCULATIONS</u> PTO USE ONLY | | |
| Basic National Fee (37 CFR 1.492(a)(1)-(5): | | | | |
| Neither international preliminary examination fee (37 CFR 1.482) Nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO (1.492(a)(3)) \$1,040 | | | | |
| International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO (1.492(a)(5)) \$890.00 | | | | |
| International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO(1.492(a)(2)) \$740.00 | | | | |
| International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) (1.492(a)(1)) \$710.00 | | | | |
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| ENTER APPROPRIATE BASIC FEE AMOUNT = \$ | | 1,040 | | |
| Surcharge of \$130.00 for furnishing the oath or declaration later than [] 20 [] 30 months from the earliest claimed priority date (37 C.F.R. 1.492(e)). | | \$ | | |
| Claims | Number Filed | Number Extra | Rate | \$ |
| Total Claims | 16 -20- | 0 | X \$ 18.00 | \$ 0 |
| Independent Claims | 2 -3- | 0 | X \$ 84.00 | \$ 0 |
| Multiple dependent claim(s) (if applicable) | | | + \$280.00 | \$ |
| TOTAL OF ABOVE CALCULATIONS = \$ | | 1,040 | | |
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| | | SUBTOTAL = \$ | 1,040 | |
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| <p>a. <input checked="" type="checkbox"/> A check in the amount of \$ 1040 & 40 to cover the above fees is enclosed.</p> <p>b. [] Please charge our Deposit Account No. 02-4377 in amount of \$ to cover the above fees. A copy of this sheet is enclosed.</p> <p>c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-4377. A copy of this sheet is enclosed.</p> | | | | |
| <p>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</p> | | | | |
| <p>SEND ALL CORRESPONDENCE TO: Ronald B. Hildreth BAKER BOTTS L.L.P. 30 Rockefeller Plaza New York, New York 10112-4498</p> | | | | |
|  Attorney: Ronald B. Hildreth PTO Reg: 19,498 19 FEBRUARY 2002 Date | | | | |

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(54) Title: PHOTORESISTIVE RESIN COMPOSITION

(57) Abstract: The present invention relates to a photosensitive resin composition capable of being developed by an alkaline aqueous solution, and provides a photosensitive resin which has superior resolving power by having a chemical bond between a binder resin and a crosslinking compound as well as a chemical bond between binder resin chains at an exposed area during an exposure process, thus maximizing a solubility difference between an exposed area and a non-exposed area during a developing process, and which has process benefits as well as superior film characteristics by reducing a consumed amount of a crosslinking compound, thus minimizing total amount of UV irradiation necessary.

PHOTOSENSITIVE RESIN COMPOSITION

CROSS REFERENCE TO RELATED APPLICATION

This application is based on Korean patent application No. 10-1999-5 0033884 filed on August 17, 1999, which is incorporated hereinto by reference.

BACKGROUND OF THE INVENTION

(a) Field of the Invention

The present invention relates to a light-sensitive resin composition capable of being developed by an alkaline aqueous solution, more particularly 10 to a photosensitive resin composition applicable to a color filter and for thin film transistor circuit passivation in the liquid crystal display manufacturing process.

(b) Description of the Related Art

Demand for photosensitive resins capable of being developed by an alkaline aqueous solution is recently increasing in many fields requiring micro 15 image formation due to the so-called photolithography technology development in which images are formed using active lights such as ultraviolet rays, etc.

Alkaline developing type photosensitive resins have been used in dry film resists for printed circuit board fabrication, photoresists for semiconductor circuit fabrication, etc., and their applications such as color filter and various 20 circuit passivation are recently being expanded into semiconductors and flat panel display fields, including liquid crystal displays.

A photosensitive resin composition capable of being developed by an alkaline aqueous solution generally comprises a) a binder resin which is dissolved or swelled by an alkaline solution; b) a crosslinking compound having 25 at least two ethylenically unsaturated bonds; c) a photopolymerization initiator; and d) a solvent capable of dissolving the above mentioned constituents, in which dyestuff, pigment, or various additives which improve the filming property or adhesive property to the substrate can be contained if necessary.

The above a), as a binder resin which is dissolved or swelled by an

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alkaline aqueous solution, generally comprising a structure containing carboxylic acid or a carboxylic acid anhydride or hydroxide group, an amino group, an amide group in the polymer chains, and a novolak based phenol resin, an acryl based resin homopolymer, or an acryl based resin copolymer, is widely used.

Particularly, an acryl based binder resin having superior transparency for visible light rays is widely being used when the photosensitive resin composition is used as a color filter and for thin film transistor circuit passivation in the flat panel display fields.

10 Copolymers using one or more compounds selected from the group consisting of acrylic acid, methacrylic acid, an alkyl ester thereof, and substituted or unsubstituted aryl esters are mainly used as acryl based binder resins soluble in the alkaline solution.

The use of benzyl acrylate/methacrylic acid copolymer is disclosed in
15 U.S. Patent Nos. 4,629,680 and 4,139,391, methyl methacrylate/2-ethylhexyl methacrylate/methacrylic acid terpolymer is disclosed in Japanese Patent Publication No. Showa 54-34327, and methyl methacrylate/ethyl acrylate/acrylic acid terpolymer is disclosed in Japanese Patent Publication No. Showa 55-6210. Furthermore, a copolymer using allylacrylate, hydroxyalkyl acrylate, methacrylic
20 acid, etc. is disclosed in Japanese Patent Laid-open Publication No. Heisei 9-23059.

A compound of the above b), as a crosslinking compound having at least two ethylenically unsaturated bonds, includes polyethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate, pentaerythritol hexa(meth)acrylate, etc.

In photosensitive resin compositions of existing technologies, this
30 crosslinking compound is simply distributed in a binder resin of the composition, and when it is exposed to an active light such as ultraviolet rays, etc., a crosslinking reaction occurs and a network structure is formed preventing an

alkaline soluble resin from dissolving by a developer in the development process, consequently playing a role in the leaving of images on a substrate.

- However, solubility differences between areas exposed to light and areas not exposed to light in existing photosensitive resin compositions are not large enough, and binder resin which should practically remain during the development process is partially dissolved by a development solution, and consequently it is difficult to obtain desirable micro patterned shapes in most cases.

- On the other hand, when crosslinking compounds are excessively used to prevent this phenomena, not only are process properties decreased by surface hardness deterioration after exposure to light, but also process yields decrease as an exposing amount to light causing sufficient crosslinking reaction increases.

- Furthermore, there is a disadvantage in this case that solubilities of the non-exposed areas are also deteriorated, thus reducing the resolving power as a resist.

SUMMARY OF THE INVENTION

- It is an object of the present invention to provide a photosensitive resin which has superior resolving power by having a chemical bond between a binder resin and a crosslinking compound as well as a chemical bond between binder resin chains at an exposed area during an exposing process, thus maximizing the solubility difference between an exposed area and a non-exposed area during the developing process, and which has process benefits as well as superior film characteristics by reducing the consumed amount of crosslinking compound, thus decreasing total exposed light quantity in order to solve the above described problems.

- The present invention provides a photosensitive resin composition comprising a self-curable binder resin, a photopolymerization initiator, a crosslinking compound having at least two ethylenically unsaturated bonds, and a solvent, wherein the self-curable binder resin is the following Chemical Formula 1:

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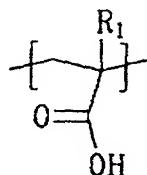
[Chemical Formula 1]

- A - B - C -

where A is a compound represented as in the following Chemical Formula 1-A;

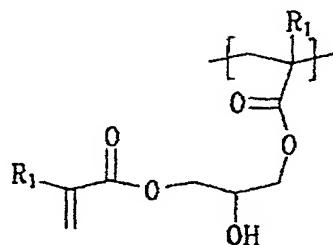
[Chemical Formula 1-A]

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B is a compound represented as in the following Chemical Formula 1-B;

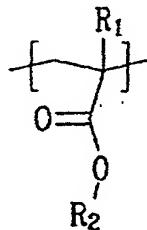
[Chemical Formula 1-B]



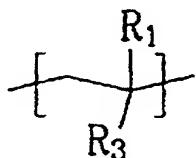
C is a compound represented as in the following Chemical Formula 1-C

10 and / or Chemical Formula 1-C';

[Chemical Formula 1-C]



[Chemical Formula 1-C']



15 wherein R₁ is H or CH₃, R₂ is an alkyl group having 1 to 8 carbon atoms, a hydroxy group substituted alkyl group, or a substituted or unsubstituted aryl group having 1 to 12 carbon atoms, and R₃ is a benzene, an alkyl group having 1 to 8 carbon atoms, an alkoxy group having 1 to 8 carbon atoms, a benzene

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having a C₁ ~ C₆ alkyl substituent, a benzene having a C₁ ~ C₈ alkoxy substituent, or a hydroxide group or a halogen substituted benzene.

The A portion in the binder resin of Chemical Formula 1 accounts for 10 to 50 mol%, the B portion accounts for 0 to 15 mol%, and the C portion 5 accounts for 50 to 90 mol% of the total binder resin.

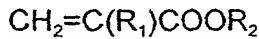
A crosslinking compound having at least two unsaturated groups can further be used in the photosensitive resin composition if necessary.

A self-curable binder resin of the Chemical Formula 1 is obtained by reacting a copolymer comprising a constituent of a compound having one or 10 more carboxylic acids selected from the group consisting of the following Chemical Formulae 2, 3, and 4 with a compound of the following Chemical Formula 5.

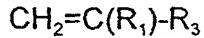
[Chemical Formula 2]



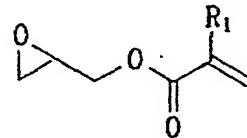
[Chemical Formula 3]



[Chemical Formula 4]



[Chemical Formula 5]



20

wherein R₁ is hydrogen or a methyl group, R₂ is a compound selected from the group consisting of an alkyl group having 1 to 8 carbon atoms, a hydroxy group substituted alkyl group, and a substituted or unsubstituted aryl group or arylalkyl group having 4 to 12 carbon atoms, and R₃ is a compound 25 selected from the group consisting of a benzene, an alkyl group having 1 to 8 carbon atoms, an alkoxy group having 1 to 8 carbon atoms, a benzene having a C₁ ~ C₆ alkyl substituent, a benzene having a C₁ ~ C₈ alkoxy substituent, and a hydroxide group or halogen substituted benzene.

A copolymer which is prepared by copolymerizing a self-curable binder

resin of the Chemical Formula 1 with one or both of a compound of the Chemical Formula 2 and a compound of the Chemical Formula 3 or Chemical Formula 4 in a certain mole ratio is put into a flask with a stirrer and a nitrogen injecting hole attached, and then dissolved using a solvent such as methyl ethyl 5 ketone, etc. A number average molecular weight of a copolymer to be used is 1,000 to 100,000 and preferably 2,000 to 30,000.

After increasing the flask temperature to 120 °C and slowly adding a compound of Chemical Formula 5 over one hour, the solution is reacted until an epoxy group is completely removed. A self-curable binder resin is prepared by 10 forming precipitates from the reactant using a mixture with a ratio of n-hexane and methanol of 1:1, and drying the precipitates under vacuum.

An epoxy group of a compound of Chemical Formula 5 is reacted with carboxylic acid existing in the binder resin and forming an ester consequently forming a self-curable binder resin, wherein a reactive (meth)acryl group is 15 employed in the linear binder resin as a branch.

This obtained self-curable binder resin, as a resin which is dissolved or at least swelled by an alkaline aqueous solution, can cause the curing reaction by using an active light such as ultraviolet rays, etc.

Furthermore, the present invention provides a photosensitive resin 20 composition prepared by mixing a copolymer in which a compound of the Chemical Formula 2 is copolymerized with one or both compounds of a compound of the Chemical Formula 3 and a compound of the Chemical Formula 4, a photopolymerization initiator, and a solvent.

While existing photosensitive resin components form a network 25 structure by chemical reactions which occurs between only crosslinking compounds each other in UV exposure process, the photosensitive resin composition of the present invention forms a network structure not only with the crosslinking compounds but also with binder resin chains. Because of this, the photosensitive resin composition of the present invention provides the 30 maximized solubility deference between an exposed area and a non exposed. Thus it can be obtained the superior film characteristics as well as the excellent

sensitivity and resolution by reducing the amount of crosslinking compound or not using it.

Acrylic acid, methacrylic acid, etc. can be used as a compound of the Chemical Formula 2, and its consumed amount is from 10 to 90 mol% based on 5 the mole sum of total monomers in the copolymer.

A compound of the Chemical Formula 3 is preferably a compound selected from the group consisting of benzyl(meth)acrylate, phenyl(meth)acrylate, cyclohexyl(meth)acrylate, methyl(meth)acrylate, ethyl(meth)acrylate, or 2-ethylhexyl(meth)acrylate, and more preferably 10 benzyl(meth)acrylate or phenyl(meth)acrylate.

A compound of the Chemical Formula 4 is preferably a compound selected from the group consisting of styrene, 4-hydroxystyrene, 4-methylstyrene, or vinyl acetate.

Furthermore, a compound of the Chemical Formula 5 is preferably 15 glycidyl acrylate or glycidyl methacrylate. This compound uses 0.1 to 90 mol% of the carboxylic acid contained monomer in Chemical Formula 2.

A crosslinking compound having at least two unsaturated groups which can be used in the present invention if necessary includes a compound selected from the group consisting of polyethylene glycol di(meth)acrylate, propylene 20 glycol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol di(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, pentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol 25 hexa(meth)acrylate, trimethylolpropane triacrylate, and a mixture thereof, and preferably includes dipentaerythritol penta(meth)acrylate and dipentaerythritol hexa(meth)acrylate.

The content of the crosslinking compound is from 0 to 200 weight%, and preferably from 0 to 150 weight%, based on the total weight of the self- 30 curable binder resin.

A photopolymerization initiator example is a compound selected from the group consisting of benzophenones such as benzophenone and

acetophenone; substituted benzophenones such as bis-4,4'-dimethylaminobenzophenone and bis-4,4'-diethylaminobenzophenone; triazine based photoinitiators such as 2,4,6-tris(trichloromethyl)-triazine; ketone based photopolymerization initiators such as N-methyl-2-benzoylmethylene- β -naphthothiazole and 2,2-dimethoxy-1,2-diphenylethanone; and a mixture thereof.

The content of the photopolymerization initiator is preferably from 0.1 to 10 weight% based on the total weight of the photopolymerizable composition.

A general solvent mainly used in the polymerization of acryl polymer, is a compound selected from the group consisting of methylethylketone, cyclohexanone, tetrahydrofurane, methyl cellosolve, methyl cellosolve acetate, dimethyl formamide, propylene glycol methylether acetate, 2-methoxyethylether, and a mixture thereof.

On the other hand, small amounts of a pigment, a dyestuff, an antifoaming agent for increasing filming properties, a surfactant, a thermal polymerization preventing agent, an adhesion promoter, etc. in addition to the above basic components can be used in a photosensitive resin composition of the present invention if necessary.

The finally obtained photosensitive resin composition solution is filtered using a membrane filter having 0.1 to 5 μm pores. This filtered resin composition is filmed using a notified method such as a spin coating method, a roll coating method, a spray coating method, etc. A glass plate or a silicone wafer can be used as a filming substrate, wherein the film surface thickness is determined by filming conditions such as composition viscosity, concentration of solid content, filming rate, etc., and a 0.1 to 500 μm thick thin film can be obtained using a composition of the present invention.

The obtained thin film is pretreated by maintaining a temperature of 50 to 150 °C at a heating plate or an oven for 10 to 500 seconds.

Ultraviolet rays are irradiated on the somewhat dried thin film through a positive type test photomask (made by Toppan Printing Co., Ltd.), wherein the ultraviolet ray light is irradiated in the intensity of illumination of from about 30 to 500 mJ/cm^2 using a 1 kW high pressure mercury lamp, etc. containing g, h, and

i lines, and particular optical filters are not used.

The solubility of the ultraviolet ray irradiated area becomes far less than that of the non-ultraviolet ray irradiated area, thus maximizing the solubility difference between them.

- 5 The ultraviolet ray irradiated thin film is developed by a spray method or a dipping method at a temperature of 20 to 30 °C, wherein a KOH aqueous solution having from 9 to 12 pH or 0.1 to 5 weight% of tetramethylammonium hydride aqueous solution can be used as a developer.

DETAILED DESCRIPTION OF THE INVENTION

- 10 In the following detailed description, only the preferred embodiments of the invention have been shown and described, simply by way of illustration of the best mode contemplated by the inventor(s) of carrying out the invention. As will be realized, the invention is capable of modification in various obvious respects, all without departing from the invention. Accordingly, the description 15 is to be regarded as illustrative in nature, and not restrictive.

- Preferable SYNTHESIZING EXAMPLES and EXAMPLES are described as follows in order to help understand the present invention. However, the following SYNTHESIZING EXAMPLES and EXAMPLES are only for help understand the present invention, and the present invention is not 20 limited to the following SYNTHESIZING EXAMPLES and EXAMPLES.

[SYNTHESIZING EXAMPLE 1]

- 10 g of copolymer in which the mole ratio of benzylmethacrylate : methacrylic acid is 60 : 40, and the number average molecular weight is 10,000 were put into a flask with a stirrer and a nitrogen injecting hole attached and 25 dissolved using 100 µm of methyl ethyl ketone. After increasing the flask temperature to 120 °C and slowly adding 0.3 g of glycidyl methacrylate over one hour, the solution was reacted until epoxy groups were completely removed. Precipitates were formed from the reactant using a mixture of a ratio of n-hexane and methanol of 1:1, and dried under vacuum thereby obtaining a 30 binder resin.

10

[SYNTHESIZING EXAMPLE 2]

A binder resin was obtained according to the method of SYNTHESISING EXAMPLE 1 except that 10 g of copolymer in which the mole ratio of benzylmethacrylate : methacrylic acid was 50 : 50 and the number average molecular weight was 15,000 were used, and 0.6 g of glycidyl acrylate were also used.

[SYNTHESIZING EXAMPLE 3]

A binder resin was obtained according to the method of SYNTHESISING EXAMPLE 1 except that 10 g of copolymer in which the mole ratio of benzylmethacrylate : methacrylic acid was 70 : 30 and the number average molecular weight was 15,000 were used, and 0.05 g of glycidyl acrylate were also used.

[SYNTHESIZING EXAMPLE 4]

A binder resin was obtained according to the method of SYNTHESISING EXAMPLE 1 except that 10 g of copolymer in which the mole ratio of benzylmethacrylate : methacrylic acid was 70 : 30 and the number average molecular weight was 10,000 were used, and 0.04 g of glycidyl acrylate were also used.

[SYNTHESIZING EXAMPLE 5]

A binder resin was obtained according to the method of SYNTHESISING EXAMPLE 1 except that 10 g of terpolymer in which the mole ratio of ethylmethacrylate : methacrylic acid : styrene was 50 : 40 : 10 and the number average molecular weight was 14,500 were used, and 0.3 g of glycidyl acrylate were also used.

[SYNTHESIZING EXAMPLE 6]

A binder resin was obtained according to the method of SYNTHESISING EXAMPLE 1 except that 10 g of terpolymer in which the mole ratio of ethylmethacrylate : methacrylic acid : styrene was 60 : 30 : 10 and the number average molecular weight was 14,500 were used, and 0.05 g of glycidyl acrylate were also used.

A photosensitive resin composition of the present invention was prepared using a binder resin prepared in the above SYNTHSIZING

EXAMPLES 1 to 6.

[EXAMPLE 1]

A photosensitive resin composition was prepared in compositions represented as in the following Table 1.

5 [Table 1]

| | |
|---|------|
| A binder resin prepared in SYNTHESIZING EXAMPLE 1 | 5 g |
| Bis-4,4'-diethylaminobenzophenone | 2 g |
| Propylene glycol methyl ether acetate | 20 g |

The above prepared composition solution was filtered using a Teflon membrane filter having 0.2 μm pores. A photosensitive resin composition was coated on a glass plate using a spin method, put on a heating plate, and 10 maintained at a temperature of 80 °C for three minutes. Subsequently, after putting a positive type test photomask (made by Toppan Printing Co., Ltd.) as a contacting method on a thin film, ultraviolet rays were irradiated thereon, wherein ultraviolet ray light was irradiated at the intensity of illumination of 100 mJ/cm² using a 1 kW high pressure mercury lamp containing g, h, and i lines, 15 and particular optical filters were not used. The ultraviolet ray irradiated thin film was developed by dipping it into a KOH aqueous solution developer having a pH of 10.5, for two minutes. After washing the thin film coated glass plate with distilled water, it was dried by blowing nitrogen gas and heated in a heating oven at 250 °C for one hour. The obtained film thickness was 3.5 μm and 20 clear patterns having 8 μm of line width and gap could be obtained.

[EXAMPLE 2]

A photosensitive resin composition was prepared in compositions represented as in the following Table 2.

[Table 2]

| | |
|---|------|
| A binder resin prepared in SYNTHESIZING EXAMPLE 2 | 5 g |
| Bis-4,4'-diethylaminobenzophenone | 2 g |
| Propylene glycol methyl ether acetate | 20 g |

A film was formed from the above prepared photosensitive resin

12

composition in a method as in EXAMPLE 1, exposed at the intensity of illumination of 100 mJ/cm^2 , and developed.

The obtained film thickness was $3.5 \mu\text{m}$ and clear patterns having $7 \mu\text{m}$ of line width and gap could be obtained.

5 [EXAMPLE 3]

A photosensitive resin composition was prepared in compositions represented as in the following Table 3.

[Table 3]

| | |
|---|------|
| A binder resin prepared in SYNTHESIZING EXAMPLE 3 | 5 g |
| Bis-4,4'-diethylaminobenzophenone | 2 g |
| Propylene glycol methyl ether acetate | 20 g |

10 A film was formed from the above prepared photosensitive resin composition in a method as in EXAMPLE 1, exposed at the intensity of illumination of 150 mJ/cm^2 , and developed.

The obtained film thickness was $4.0 \mu\text{m}$ and clear patterns having $9 \mu\text{m}$ of line width and gap could be obtained.

15 [EXAMPLE 4]

A photosensitive resin composition was prepared in compositions represented as in the following Table 4.

[Table 4]

| | |
|---|------|
| A binder resin prepared in SYNTHESIZING EXAMPLE 4 | 4 g |
| Bis-4,4'-diethylaminobenzophenone | 2 g |
| Propylene glycol methyl ether acetate | 30 g |
| Pentaerythritol tetramethacrylate | 4 g |

20 A film was formed from the above prepared photosensitive resin composition in a method as in EXAMPLE 1, exposed at the intensity of illumination of 150 mJ/cm^2 , and developed.

The obtained film thickness was $4.5 \mu\text{m}$ and clear patterns having $8 \mu\text{m}$ of line width and gap could be obtained.

25 [EXAMPLE 5]

A photosensitive resin composition was prepared in compositions represented as in the following Table 5.

[Table 5]

| | |
|---|------|
| A binder resin prepared in SYNTHESIZING EXAMPLE 5 | 5 g |
| Bis-4,4'-diethylaminobenzophenone | 2 g |
| Propylene glycol methyl ether acetate | 20 g |

5 A film was formed from the above prepared photosensitive resin composition in a method as in EXAMPLE 1, exposed at the intensity of illumination of 150 mJ/cm², and developed.

The obtained film thickness was 3.8 μm and clear patterns having 9 μm of line width and gap could be obtained.

10 [EXAMPLE 6]

A photosensitive resin composition was prepared in compositions represented as in the following Table 6.

[Table 6]

| | |
|---|------|
| A binder resin prepared in SYNTHESIZING EXAMPLE 6 | 5 g |
| Bis-4,4'-diethylaminobenzophenone | 3 g |
| Propylene glycol methyl ether acetate | 40 g |
| Pentaerythritol tetraacrylate | 2 g |

15 A film was formed from the above prepared photosensitive resin composition in a method as in EXAMPLE 1, exposed at the intensity of illumination of 100 mJ/cm², and developed.

The obtained film thickness was 3.1 μm and clear patterns having 7 μm of line width and gap could be obtained.

20 [EXAMPLE 7]

A photosensitive resin composition was prepared in compositions represented as in the following Table 7. A photosensitive resin composition was prepared not by synthesizing a binder resin first, but by putting the starting material together with constituents comprising the photosensitive resin composition in the present EXAMPLE 7, different from the above EXAMPLES.

[Table 7]

| | |
|--|--------|
| Benzylmethacrylate/methacrylic acid copolymer (mole ratio = 60/40, number average molecular weight = 10000) | 5 g |
| Glycidyl methacrylate | 0.15 g |
| Bis-4,4'-diethylaminobenzophenone | 2 g |
| Propylene glycol methyl ether acetate | 20 g |

A film was formed from the above prepared photosensitive resin composition in a method as in EXAMPLE 1, exposed at the intensity of 5 illumination of 150 mJ/cm^2 , and developed.

The obtained film thickness was $3.6 \mu\text{m}$ and clear patterns having $8 \mu\text{m}$ of line width and gap could be obtained.

[COMPARATIVE EXAMPLES 1 to 3]

A photosensitive resin composition was prepared in compositions 10 represented as in the following Table 8.

[Table 8]

| | |
|--|------|
| Benzylmethacrylate/methacrylic acid copolymer (mole ratio = 70/30, number average molecular weight = 10000) | 5 g |
| Pentaerythritol tetra(meth)acrylate | 5 g |
| Bis-4,4'-diethylaminobenzophenone | 2 g |
| Propylene glycol methyl ether acetate | 40 g |

The results were obtained as in the following Table 9 by forming patterns as changing exposed light quantity after forming a film using the above 15 obtained photosensitive resin composition in a method as in EXAMPLE 1.

[Table 9]

| Classification | COMPARATIVE EXAMPLE 1 | COMPARATIVE EXAMPLE 2 | COMPARATIVE EXAMPLE 3 |
|------------------------|-----------------------|-----------------------|-----------------------|
| Exposed light quantity | 100 mJ/cm^2 | 150 mJ/cm^2 | 200 mJ/cm^2 |
| Film thickness | - | $3.0 \mu\text{m}$ | $3.8 \mu\text{m}$ |
| Resolving power | Pattern lost | $20 \mu\text{m}$ | $10 \mu\text{m}$ |

According to the results obtained from EXAMPLES 1 to 7, in the case of

forming a thin film using a photosensitive resin composition using a self-curable binder resin prepared in accordance with the present invention, the obtained thin film thickness was 3 to 5 μm and clear patterns having 7 to 9 μm of line width and gap could be obtained when the exposed light quantity was irradiated
5 at the intensity of illumination of 100 to 150 mJ/cm^2 .

On the contrary, patterns themselves were lost when the exposed light quantity was 100 mJ/cm^2 in the case of photosensitive resin compositions of COMPARATIVE EXAMPLES 1 to 3 in which self-curable binder resins were not used, and the thin film thickness was 3.0 to 3.8 μm , and the line width and gap
10 were decreased from 20 μm to 10 μm when the exposed light quantity was increased to 150 to 200 mJ/cm^2 . Therefore, it can be seen that clear patterns can be obtained as the exposed light quantity increases in the case of a photosensitive resin composition in which a self-curable binder resin is not used, and the increase of exposed light quantity means an increase in process time.
15 Furthermore, it can be seen that clearer and finer patterns than the results of EXAMPLES according to the present invention could not be obtained since the thickness of the thin film pattern was represented as 3.8 μm and the line width and gap were represented as 10 μm even when the exposed light quantity was 200 mJ/cm^2 .

20 Therefore, the present invention can provide a photosensitive resin composition having process benefits, and superior resolving power and film properties since although less exposed light quantity is applied, a photosensitive resin composition using a self-curable binder resin can obtain much clearer and finer patterns compared with existing compositions, thus
25 shortening time of UV exposure process.

While the present invention has been described in detail with reference to the preferred embodiments, those skilled in the art will appreciate that various modifications and substitutions can be made thereto without departing from the spirit and scope of the present invention as set forth in the appended claims.

WHAT IS CLAIMED IS:

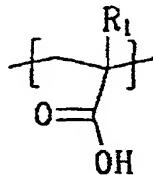
1. A photosensitive resin composition comprising a self-curable binder resin, a crosslinking compound having at least two ethylenically unsaturated bonds, a photopolymerization initiator, and a solvent, wherein the
 5 self-curable binder resin is a compound represented as in the following Chemical Formula 1:

[Chemical Formula 1]

- A - B - C -

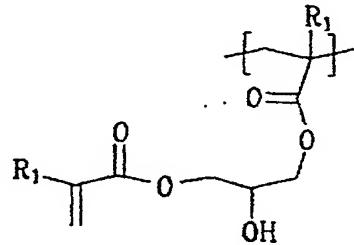
10 where A is a compound represented as in the following Chemical Formula 1-A;

[Chemical Formula 1-A]



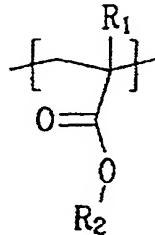
where B is a compound represented as in the following Chemical Formula 1-B;

15 [Chemical Formula 1-B]

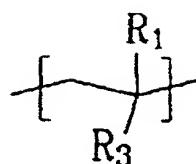


where C is a compound represented as in the following Chemical Formula 1-C and/or Chemical Formula 1-C';

[Chemical Formula 1-C]



[Chemical Formula 1-C']

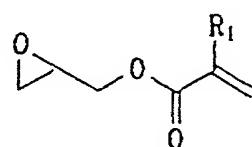


- wherein R_1 is H or $-CH_3$, R_2 is an alkyl group having 1 to 8 carbon atoms, a hydroxyl group substituted alkyl group, or a substituted or unsubstituted aryl group having 1 to 12 carbon atoms, and R_3 is a benzene, an alkyl group having 1 to 8 carbon atoms, an alkoxy group having 1 to 8 carbon atoms, a benzene having a $C_1 \sim C_6$ alkyl substituent, a benzene having a $C_1 \sim C_8$ alkoxy substituent, or a hydroxide group or halogen substituted benzene.

2. A photosensitive resin composition in accordance with claim 1,
10 wherein an A portion in a binder resin of the Chemical Formula 1 accounts for 10 to 50 mol%, a B portion accounts for 0 to 15 mol%, and a C portion accounts for 90 to 50 mol% based on the total binder resin.

3. A photosensitive resin composition in accordance with claim 1,
wherein the self-curable binder resin is a self-curable binder resin obtained by
15 reacting a copolymer which is prepared by copolymerizing a compound of the following Chemical Formula 2 with one or both of a compound of the following Chemical Formula 3 and a compound of the following Chemical Formula 4 with a compound of the following Chemical Formula 5:

- [Chemical Formula 2]
20 $CH_2=C(R_1)COOH$
[Chemical Formula 3]
 $CH_2=C(R_1)COOR_2$
[Chemical Formula 4]
 $CH_2=C(R_1)-R_3$
25 [Chemical Formula 5]



wherein R_1 is hydrogen or a methyl group, R_2 is a compound selected

from the group consisting of an alkyl group having 1 to 8 carbon atoms, a hydroxy group substituted alkyl group, and a substituted or unsubstituted aryl group or arylalkyl group having 4 to 12 carbon atoms, and R₃ is a compound selected from the group consisting of a benzene, an alkyl group having 1 to 8 carbon atoms, an alkoxy group having 1 to 8 carbon atoms, a benzene having a C₁ ~ C₆ alkyl substituent, a benzene having a C₁ ~ C₈ alkoxy substituent, and a hydroxide group or halogen substituted benzene.

4. A photosensitive resin composition in accordance with claim 3, wherein a compound of the Chemical Formula 2 comprising the copolymer is acrylic acid or methacrylic acid, a compound of the Chemical Formula 3 is a compound selected from the group consisting of benzyl(meth)acrylate, phenyl(meth)acrylate, cyclohexyl(meth)acrylate, methyl(meth)acrylate, ethyl(meth)acrylate, and 2-ethylhexyl(meth)acrylate, and a compound of the Chemical Formula 4 is a compound selected from the group consisting of styrene, 4-hydroxystyrene, 4-methylstyrene, and vinyl acetate.

5. A photosensitive resin composition in accordance with claim 3, wherein a compound of the Chemical Formula 5 is glycidyl acrylate or glycidyl methacrylate.

6. A photosensitive resin composition in accordance with claim 3, wherein a number average molecular weight of the copolymer is from 1,000 to 100,000.

7. A photosensitive resin composition in accordance with claim 3, wherein a compound amount of the Chemical Formula 5 is from 0.1 to 90 mol% based on a carboxylic acid containing monomer of Chemical Formula 2 in a binder resin of Chemical Formula 1.

8. A photosensitive resin composition in accordance with claim 3, wherein a compound amount of the Chemical Formula 2 is from 10 to 90 mol% based on the mole sum of Chemical Formulae 2, 3, and 4.

9. A photosensitive resin composition in accordance with claim 1, further comprising a crosslinking compound having at least two unsaturated groups.

10. A photosensitive resin composition in accordance with claim 9,

wherein the crosslinking compound is a compound selected from the group consisting of polyethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol di(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, pentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate, trimethylolpropane triacrylate, and a mixture thereof.

11. A photosensitive resin composition in accordance with claim 9,
10 wherein the crosslinking compound amount is from 0 to 200 weight% based on
the self-curable binder resin of Chemical Formula 1.

12. A photosensitive resin composition prepared by mixing a copolymer which is prepared by copolymerizing a compound of the following Chemical Formula 2 and one or both of a compound of the following Chemical
15 Formula 3 and a compound of the following Chemical Formula 4 with a compound of the following Chemical Formula 5, a photoinitiator, and a solvent:

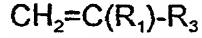
[Chemical Formula 2]



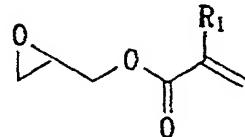
[Chemical Formula 3]

20 $\text{CH}_2=\text{C}(\text{R}_1)\text{COOR}_2$

[Chemical Formula 4]



[Chemical Formula 5]



25 wherein R_1 is hydrogen or methyl group, R_2 is a compound selected from the group consisting of an alkyl group having 1 to 8 carbon atoms, a hydroxy group substituted alkyl group, and a substituted or unsubstituted aryl group or arylalkyl group having 4 to 12 carbon atoms, and R_3 is a compound selected from the group consisting of a benzene, an alkyl group having 1 to 8

20

carbon atoms, an alkoxy group having 1 to 8 carbon atoms, a benzene having a C₁ ~ C₆ alkyl substituent, a benzene having a C₁ ~ C₈ alkoxy substituent, and a hydroxide group or halogen substituted benzene.

13. A photosensitive resin composition in accordance with claim 12,
5 wherein a compound of the Chemical Formula 2 comprising the copolymer is
acrylic acid or methacrylic acid, a compound of the Chemical Formula 3 is a
compound selected from the group consisting of benzyl(meth)acrylate,
phenyl(meth)acrylate, cyclohexyl(meth)acrylate, methyl(meth)acrylate,
ethyl(meth)acrylate, and 2-ethylhexyl(meth)acrylate, and a compound of the
10 Chemical Formula 4 is a compound selected from the group consisting of
styrene, 4-hydroxystyrene, 4-methylstyrene, and vinyl acetate.

14. A photosensitive resin composition in accordance with claim 12,
wherein a compound of the Chemical Formula 5 is glycidyl acrylate or glycidyl
methacrylate.

15. 15. A photosensitive resin composition in accordance with claim 12,
wherein a number average molecular weight of the copolymer is from 1,000 to
100,000.

16. A photosensitive resin composition in accordance with claim 12,
wherein a compound amount of the Chemical Formula 2 is from 10 to 90 mol%
20 based on the mole sum of Chemical Formulae 2, 3, and 4.

5
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(54) Title: PHOTORESISTIVE RESIN COMPOSITION

(57) Abstract: The present invention relates to a photosensitive resin composition capable of being developed by an alkaline aqueous solution, and provides a photosensitive resin which has superior resolving power by having a chemical bond between a binder resin and a crosslinking compound as well as a chemical bond between binder resin chains at an exposed area during an exposure process, thus maximizing a solubility difference between an exposed area and a non-exposed area during a developing process, and which has process benefits as well as superior film characteristics by reducing a consumed amount of a crosslinking compound, thus minimizing total amount of UV irradiation necessary.

COMBINED DECLARATION
AND POWER OF ATTORNEY

(Original, Design, National Stage of PCT, Divisional, Continuation or C-I-P Application)
My residence, post office address and citizenship are as stated below next to my name; I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

PHOTOSENSITIVE RESIN COMPOSITION

This declaration is of the following type:

- original
- design
- national stage of PCT.
- divisional
- continuation
- continuation-in-part (C-I-P)

the specification of which: (complete (a), (b), or (c))

- (a) is attached hereto.
- (b) was filed on as Application Serial No. _____ and was amended on (if applicable).
- (c) was described and claimed in PCT International Application No. PGT/KR00/00883 filed on August 10, 2000 and was amended on (if applicable).

Acknowledgement of Review of Papers and Duty of Candor

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of the subject matter claimed in this application in accordance with Title 37, Code of Federal Regulations § 1.56.

In compliance with this duty there is attached an information disclosure statement.
37 CFR 1.98.

Priority Claim

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT International Application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign applications for patent or inventor's certificate or any PCT International Application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application on which priority is claimed

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- (d) no such applications have been filed.
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→

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FILE NO.:

| PRIOR FOREIGN/PCT APPLICATION(S) FILED WITHIN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO SAID APPLICATION | | | |
|--|-----------------|--------------------------------------|---|
| COUNTRY | APPLICATION NO. | DATE OF FILING (day, month, year) | DATE OF ISSUE (day, month, year) |
| Korea | 1999-33884 | 17/08/99 | <input checked="" type="checkbox"/> YES NO <input type="checkbox"/> <input type="checkbox"/> YES NO <input type="checkbox"/> <input type="checkbox"/> YES NO <input type="checkbox"/> |
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Claim for Benefit of Prior U.S. Provisional Application(s)

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

| Provisional Application Number | Filing Date |
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(complete this part only if this is a divisional, continuation or C-I-P application)

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(Application Serial No.) (Filing Date) (Status) (patented, pending, abandoned)

(Application Serial No.) (Filing Date) (Status) (patented, pending, abandoned)

Power of Attorney

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| | | | | |
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| DATE | SIGNATURE OF INVENTOR <i>Yong Sik Ahn</i> | | | |
| 04/02/02 | | | | |

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| 04/02/02 | | | | |

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| 04/02/02 | | | | |

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